### **ENGINEERING DESIGN FILE (EDF)**

EDF No.: EDF-4885 EDF Rev. No.: Revision 1 Project File No.: 22901

431.02 01/30/2003 Rev. 11

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1.	Title:	Reev Data	aluatio	on of Charact	teristic Toxic	ity Des	signat	ion for V-	Tank W	/aste, U	sing Exis	sting	Sample 
2.	Index	Codes	3:										
	Buildi	ng/Typ	e <u>V-</u>	Tanks	SSC ID V	-Tank	Cons	olidated V	<u> Vaste</u>	Site Ar	ea <u>WAG</u>	1 0	J 1-10
3.	NPH	Perforr	mance	Category: _	or	<b>X</b> 1	N/A						
4.	EDF :	Safety	Categ	ory:	or	<b>X</b> 1	N/A	SCC Sa	fety Ca	tegory:		or	⊠ N/A
5.	Efforts are currently being planned to remediate the Intermediate Level Radioactive Waste tank system (commonly referred to as V-tanks) within Technical Support Facilities (TSF) 09 and 18, of Waste Area Group (WAG) 1. The Record of Decision (ROD) Amendment for the V-Tanks (entitled Record of Decision Amendment for the V-Tanks [TSF-09 and TSF-18] and Explanation of Significant Differences for the PM-2A Tanks [TSF-26] and TSF-06, Area 10, at Test Area North, Operable Unit 1-10 [DOE/ID, February 2004]) requires remediation of the V-tank waste via chemical oxidation/reduction. The chemically oxidized/reduced waste is then stabilized in a manner that meets both Land Disposal Restrictions (LDRs) and the Waste Acceptance Criteria [WAC] required for its ultimate disposal at the Idaho CERCLA Disposal Facility [ICDF]).												
	The V-tank waste is F001-listed. The OU 1-10 ROD Amendment requires treatment for all of the F001 constituents. Previous reviews of available analytical data have been insufficient to conclusively eliminate the application of "D" characteristic codes for specific organic constituents where detection limits exceeded the regulatory level. This EDF reevaluates the analytical information available in order to determine whether the V-tank waste should be designated as a non-characteristic waste. Determining that the waste is non-characteristic would focus treatment on the destruction of F-listed chlorinated solvents and Polychlorinated Biphenyls known to be present in the waste, rather than organic compounds that could theoretically exist only at concentrations below the analytical detection limits.												
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### **ENGINEERING DESIGN FILE (EDF)**

ED	F No.:	EDF-48	85	EDF Rev. No.: F	Revision 1	Proj	ect File No.: 22901	
1.	Title:	Reevalu Data	uation of Charac	teristic Toxicity De	esignation for	· V-Tank W	/aste, Using Existino	Sample
2.	Index	Codes:						
	Buildi	ng/Type	V-Tanks	SSC ID <u>V-Tanl</u>	c Consolidate	ed Waste	Site Area WAG 1 0	OU 1-10
7.	Distrib (Name Stop)	ution: and Mail						
8.	Does	document	contain sensitive	unclassified informa	tion?	☐ Yes	⊠ No	
	If Yes,	what cate	gory:					
9.	Can do	ocument b	e externally distrib	outed?		☐ No		
10.	Unifor	m File Cod	le:		Disposition	n Authority:		
	Record	d Retention	n Period:					
11.	For QA	A Records	Classification On	ly: Lifetin	ne 🗌 Noi	npermanen	t Permanent	
	Item a	nd activity	to which the QA	Record apply:				
		elated?	☐ Yes					
13.	Regist	ered Profe	essional Engineer'	s Stamp (if required	)			

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#### **ACRONYMS**

**ATSDR** Agency for Toxic Substances and Disease Registry

CERCLA Comprehensive Environmental Response, Compensation, and Liability Act

**CFR** Code of Federal Regulations

**COPC** Contaminant of Potential Concern

**DOE/ID** Department of Energy, Idaho Operations Office

**EDF** Engineering Design File

**EPA** Environmental Protection Agency

**EQL** Estimated Quantitation Limit (same as RDL)

ICDF INEEL CERCLA Disposal Facility

**INEEL** Idaho National Engineering and Environmental Laboratory

**LDR** Land Disposal Restriction

MDL Minimum Detection Level

**OU** Operable Unit

**PCB** Poly-Chlorinated Biphenyl

**PCE** Tetrachloroethylene (also called perchloroethene, tetrachloroethene, or perchloroethylene)

**RCRA** Resource Conservation and Recovery Act

**RDL** Reported Determination Level (same as EQL)

**ROD** Record of Decision

**SVOC** Semi-Volatile Organic Contaminant

**TAN** Test Area North

TCE Trichloroethylene (also call trichloroethene)

**TCLP** Toxicity Characteristic Leaching Procedure

**TSF** Technical Support Facility

**UHC** Underlying Hazardous Constituent

**VOC** Volatile Organic Contaminant

WAC Waste Acceptance Criteria

WAG Waste Area Group

# Reevaluation of Characteristic Toxicity Designation for V-Tank Waste, Using Existing Sample Data

### 1. INTRODUCTION

Efforts are currently being planned to remediate the Intermediate Level Radioactive Waste tank system (commonly referred to as V-tanks) within Technical Support Facilities (TSF)-09 and -18, of Waste Area Group (WAG) 1. The remediation is a major part of WAG 1 Environmental Remediation activities within Test Area North (TAN) of the Idaho National Engineering and Environmental Laboratory (INEEL), and is covered by the Record of Decision (ROD) Amendment for WAG 1 cleanup, which was written in accordance with the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The ROD Amendment for the V-tanks (entitled Record of Decision Amendment for the V-Tanks [TSF-09 and TSF-18] and Explanation of Significant Differences for the PM-2A Tanks [TSF-26] and TSF-06, Area 10, at Test Area North, Operable Unit 1-10 [DOE-ID, February 2004]) specifies remediation of the V-tank waste stream via chemical oxidation/reduction followed by stabilization. The chemical oxidation/reduction and stabilization process is required to meet the Land Disposal Restrictions (LDRs) treatment standard for all F001 constituents as well as the Idaho CERCLA Disposal Facility (ICDF) Waste Acceptance Criteria [WAC] for the waste's ultimate disposal. The ROD Amendment also requires an evaluation to determine if the waste exhibits the toxicity characteristic and should be classified as a RCRA characteristic waste under 40 CFR 261.24.

The waste in the V-tanks was generated over approximately 30 years of operation from the 1950s to the early 1980s. The waste in the tanks is primarily the result of decontamination operations at TAN 607 Decontamination Shop. Waste streams from other sources included the Hot Shop, Hot Cells, and IET. The waste has been classified as an F001 waste based upon historical knowledge of the use of trichloroethylene for its solvent properties. Previous reviews of available data have been insufficient to conclusively state that the waste in the V-tanks was either characteristic or non-characteristic. This EDF has determined that the waste in the V-tanks should not be considered as a characteristic waste.

#### 2. APPROACH TO CHARACTERISTIC EVALUATION

Wastes exhibit the toxicity characteristic when they leach specific contaminants above specified levels such that they become a threat to human health and the environment. There are three common approaches to determining whether waste will exceed the toxicity characteristic:

- Waste generators may use the Toxicity Characteristic Leaching Procedure (TCLP) EPA Method 1311:
- Generators may use process knowledge to say that specific constituents are or are not present above characteristic levels; or

• Generators may use analytical data that provides the total concentration of a specific constituent which can then be used to calculate the maximum leaching potential of that constituent for the waste. EPA's "rule of 20" is used to arrive at the theoretical maximum TCLP leachate concentrations for the V-tank waste.

EPA lists 40 specific contaminants in 40 CFR 261.24 that may cause a waste to fail the toxicity characteristic. These constituents are typically grouped as eight metals, six herbicides and pesticides, and 26 toxic organics. Of the 40 constituents, 20 of the constituents (all eight metals and 12 toxic organics) have been shown by analytical evidence to not exceed characteristic levels in V-tank wastes. The eight metals are: arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. The 12 toxic organics include: chlordane, chlorobenzene, chloroform, o-cresol, m-cresol, p-cresol, total cresols, p-dichlorobenzene, heptachlor, methyl ethyl ketone, pentachlorophenol, and 2,4,5 trichlorophenol.

In addition, existing process knowledge on V-tank waste has previously been used to eliminate the six herbicides and pesticides from further consideration. These six include: endrin, lindane, methoxychlor, toxaphene, 2,4-dichlorophenoxyacetic acid, and silvex. Finally, the Operable Unit (OU) 1-10 ROD Amendment specifies that the V-tank waste must be treated to meet the LDR F001 treatment standards all of the F001 listed constituents. The F001 treatment standard includes three of the toxic organic contaminants from the characteristic list of 40 (i.e., trichloroethylene [TCE], tetrachloroethylene [PCE], and carbon tetrachloride) as well as 1,1,1-trichloroethane, methylene chloride, and the chlorinated fluorocarbons 1,1,2-trichloro-1,2,2-trifluoroethane and trichloro-fluoromethane that are not subject to the characteristic determination. Hazardous constituents that are specifically addressed by a listed waste treatment standard (as specified in the OU 1-10 ROD Amendment) are exempted from being considered in the rationale for classifying a waste as characteristically toxic.

This leaves eleven constituents that have been previously cited as having insufficient information to accurately determine the need for a characteristic code. The eleven constituents include four volatile organic contaminants (VOCs) and seven semi-volatile organic contaminants (SVOCs). The four VOC constituents include benzene; 1,1-dichloroethene; 1,2-dichloroethane; and vinyl chloride. The seven SVOC constituents include 2,4-dinitrotoluene; hexachlorobenzene; hexachlorobutadiene; hexachloroethane; nitrobenzene; pyridine; and 2,4,6-trichlorophenol. These eleven contaminants of potential concern (COPCs) are the subject of this Engineering Design File (EDF). The EDF will provide a basis for determining whether or not these eleven constituents could reasonably be expected to be present and leachable in sufficient concentrations to cause the waste to exhibit the characteristic of toxicity.

The initial characteristic evaluations in EDF-3795 were unable to eliminate the eleven previously mentioned organic TCLP constituents. As a result, the V-tanks waste was presumed to carry tentative "D" characteristic codes for these eleven constituents, until such time as further evaluations were conducted. The presumption that V-tank waste is characteristically hazardous would require V-tank waste treatment for these eleven compounds plus all underlying hazardous constituents (UHCs) that may be present in the waste. Primary UHCs that would be included in a characteristic-waste treatment include: bis-2-ethylhexylphthalate (with a concentration-based treatment standard of 28 mg/kg), polychlorinated biphenyls (PCBs, with a concentration-based treatment standard of 10 mg/kg), cadmium (with a TCLP treatment standard of 0.025

An EPA interpretation stating that a dilution factor of 20 can be applied, conservatively, to the actual concentration of a sludge-component, to determine the maximum potential leachate concentrations of each component so as to mimic the actual TCLP analyses, were it to be performed.

mg/L). Irrespective of whether the waste is characteristic and subject to the UTS, the ROD Amendment requires that PCBs be treated sufficiently to demonstrate that no unreasonable risk to human health and the environment.

This EDF presents the reevaluation of this data to determine if that presumption on the concentration and leachability of the 11 remaining organic COPCs is justified. The approach in this EDF utilizes an indepth review of the analytical data available with specific emphasis on the information that can be gained by using minimum detection levels (MDLs) instead of reported determination levels (RDLs) to define hazardous concentrations, as well as an increased use of process knowledge. This reevaluation supports a refined hazardous waste determination, using either actual MDL data (when available) or conservatively derived MDL data (when referenced data is not available). Process knowledge is then used on those constituents where MDL data is insufficient to eliminate the characteristic determination. The reevaluation is broken down into separate sections on VOCs and SVOCs.

Based upon the information submitted in this EDF, the project believes that sufficient information is now available to remove the presumption of the V-tanks waste being characteristic and that the waste should be managed solely as an F001-listed waste.

#### 3. ASSUMPTIONS

- It is assumed that the previous samplings of the V-tanks that are used in this analysis (from 1993 and 1996 sampling efforts) adequately represent the composition of various contaminants.
- It is assumed that MDLs can be used instead of RDLs to conservatively estimate the concentration of various organic COPCs. The basis for this assumption is that current data validation process currently provides for the use of a "J" flag (estimated concentration) when the measured concentration is above the MDL but below the RDL. It is reasonably assumed that "U" flagged data (data that does not have a "J" flag) should be estimated as less than or equal to MDL concentration since if it were above the MDL, a "J" flag would have been added. INEEL data validation processes required the laboratory to report the value of "U" flagged data at the RDL, even though this represents an extremely over-conservative estimate of the maximum concentration. MDLs that are used for each organic COPC incorporate actual sampling, dilution and extraction ratios.
- It is reasonable and appropriate to use MDLs for "U" flagged data identified in the previous assumption for purposes of estimating the maximum TCLP concentration. For supernatant samples, the MDL serves as the actual TCLP concentration for that sample. For sludge samples, the TCLP concentration is determined by dividing the MDL by 20 L/kg for each COPC in the sludge. Such dilutions are in accordance with TCLP procedures.
- For certain V-tank sample analyses, where the defined MDLs can not be located or are not available anymore (due to incomplete referencing of such data), it is conservatively assumed that the actual MDLs for such contaminants are no more than 20% of (or five times less than) the RDL for that contaminant. This assumption is based on the SW846 definition of the Estimated Quantitation Limit (EQL), which states that the EQL (same as the INEEL RDL) is generally 5-10 times the MDL (EPA 1992). Referenced MDLs are not available for either the V-9 supernatant SVOC samples, or the VOC samples.
- Contaminants that are identified as product contaminants in materials used at TAN are assumed to be subject to the same dilution factors that the primary product has experienced during the waste generation and accumulation process at TAN.

• The degree of proof necessary to determine whether or not a waste is non-characteristic is much less critical when the waste has already been determined to be a listed waste such as the V-tanks waste. EPA recognized the difficulty in making the characteristic determination for wastes containing oils and solvents and the inherent problems with obtaining analytical information below the regulatory level and suggests relying on process knowledge when available. The following quote is form an EPA letter from Alec McBride to Richard Leonard dated March 25, 1991:

"Please note that in the case of liquid organic wastes, it is possible that these wastes may already be hazardous by virtue of a hazardous waste listing (e.g., spent solvents, hazardous wastes codes F001 -F005), in which case the hazardous waste determination with respect to the TC becomes much less critical (e.g., You would be determining if additional wastes codes applied to the waste instead of making the critical hazardous waste determination)."

### 4. REVALUATION METHODOLOGY

The initial part of the reevaluation will focus on identifying all data associated with each of the eleven organic COPCs currently identified as potentially having waste concentrations that could not be proven as less than TCLP levels. The tables will provide information on:

- Original concentrations that were used for COPCs in the sludge phases and supernatant phases of each V-tank in EDF-3868 (which were primarily based on average detection limit concentrations [from one to five samples were taken for each phase]);
- Corrected MDLs for each COPC within each V-tank phase (when available); and
- Conservatively estimated MDLs (based upon minimum RDLs) for each COPC within each V-tank phase, when referenced MDLs are not available.

From this presentation, the most appropriate concentration from these data points shall be selected to represent the lowest defensible maximum concentration of each COPC within each V-tank phase. The lowest defensible maximum concentration used in this EDF is based upon the MDLs. For total sludge concentrations, the "rule of 20" is used to calculate a worst-case TCLP maximum potential leachate concentration, using the MDLs for each COPC. This maximum potential leachate concentration is then compared to the regulatory limit.

MDLs are defined as the minimum concentrations achievable for various constituents by a particular analytical instrument. The MDLs are derived statistically for each instrument, by comparing measured analytical values for each constituent with the so-called "noise" range for that instrument (the range where analytical measurements are useless, because of instrument variations). Because of their relatively low value, and variance from machine to machine (depending on "noise" ranges for each machine), the calibration ranges for a particular instrument are generally set at a range with a minimum that is five to ten times higher than that of the machine's MDL. The bottom of the calibration range for a particular constituent is generally defined as the constituent's RDL (or EOL).

Rationale for using MDLs as the preferred concentration estimates for the organic COPCs is shown in Figure 1 of the EDF. Figure 1 identifies the various results of analysis that a constituent may demonstrate during analysis. In the first sample line, the constituent is above detection levels but at a concentration exceeding the calibration range of the constituent. In cases like these, an "E" flag is typically attached to the data, implying that the measured concentration exceeds the calibration range of the constituent. To get an accurate measurement of constituent concentration, it is necessary to dilute the sample sufficiently

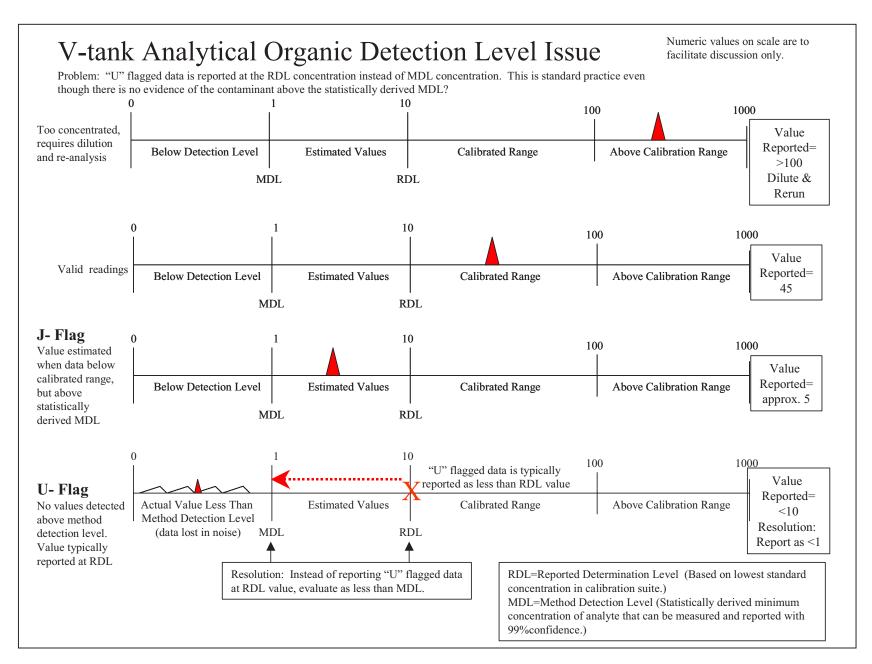


Figure 1. Comparison of Flagged Data Reporting Values

to have the measured sample be analyzed within the calibration range of that constituent. Although the data is flagged, the data is still useful from the point of view that true concentration is known to exceed the upper limit of the calibration range.

The second line in Figure 1 shows a sample that has been analyzed within the calibration range of the constituent and that provides a valid estimate of that constituent's true concentration. The bottom end of this calibration range is identified as the Reported Determination Level (RDL) for the constituent. The RDL (also called the EQL by EPA) is defined as the minimum concentration that is sufficiently above the MDL to provide an accurate determination of constituent concentration. It is for this reason that any contaminants with measured concentrations above the RDL (but within the calibration range for the constituent) are reported without any data flags (unless there are other problems identified by the analysis).

In the third line of the Figure 1, the sample is above the MDL, but below the RDL of the constituent. In cases like these, the analysis provides an estimated measure of the particular constituent at a level below the calibration range such that it cannot be quantified to the same quality level as those constituents with concentrations above the RDL. It is for this reason that all constituents with measured concentrations between the RDL and the MDL are "J'-flagged. Although the "J"-flagged data is outside of the calibration range, it is generally accepted for use as an estimate of the true concentration.

In the fourth line of Figure 1, the sample is below the MDL for a particular contaminant, and cannot be accurately measured. In this case, the standard convention is to identify this data with a "U" flag, while reporting it at the RDL concentration for that constituent. However, use of RDL values to evaluate this data (as has been done in the past) is unduly conservative. The "U"-flag is attached when the concentration is below the level at which a "J"-flag would be used to estimate the concentration. It is reasonable and appropriate to estimate the concentration of "U"-flagged data at the lower end of the "J"-flagged range that is the MDL. Realistically speaking "U"-flagged data for a COPC means the waste could contain that COPC at any concentration below the MDL. Assuming the concentration of the COPC is less than the MDL concentration is still conservative. If the data indicates that the constituent measurement is below its MDL, it stands to reason that MDLs can be used instead of RDLs to evaluate "undetected" organic contaminant concentrations, while still maintaining a conservatively high estimate. This EDF is primarily based upon use of MDLs.

Unfortunately, referenced MDLs were not available for all of the analytical V-tank data used in this reevaluation. This is because MDLs are not generally of particular concern if other hazardous organic COPCs have been identified in the waste. However, MDLs on "undetected" organic COPCs are important in this evaluation, since the only organic COPCs detected in V-tank waste are either F001-listed (TCE) or covered under the F001-treatment standards (PCE and TCA), and therefore not part of the characteristic waste evaluation. For those organic COPCs without any referenced MDLs, the reevaluation methodology calls for estimated MDLs to be used. According to SW846, the MDL for a particular constituent is typically defined at a concentration that is five to ten times less than that of the EQL (or RDL) for that constituent (EPA 1992). Therefore, estimating the MDLs conservatively at 20% of the minimum RDL for a particular constituent is appropriate when either referenced MDLs are not available, or insufficient data exists to offer a better MDL estimate.

The next part of the evaluation focuses on combining the lowest defensible maximum concentration data (MDLs either referenced or estimated) with the identified volumes of each V-tank phase to arrive at an overall estimate of the TCLP concentration for each COPC that would result from the entire waste stream. As previously stated, this data evaluation is broken down into separate sections for VOC COPCs and SVOC COPCs. The calculations used to define TCLP levels for the various organic COPCs in the V-tank sludge mimics the same procedures as are applied in the VOC and SVOC analyses and the

procedures associated with a TCLP test. This includes identification of the amount of sample volume taken (compared to standard sample volumes), the volume of the resulting concentrated sample (compared to standard sample concentrations) and the percent solids in the sludge sample, and the degree of dilution needing to be applied to SVOC data. It also includes information on the dilution required for each VOC sample, so that the same dilutions can be applied to the new VOC data. Finally, the volume of the sludge samples is used to define the mass of sludge sample that is to be multiplied by twenty, during a TCLP dilution (if total concentration data is used instead of actual TCLP data).

The resulting TCLP estimate for each organic COPC in the V-tank waste is then compared with the TCLP regulatory level, as the initial screen in the overall evaluation. Those organic COPCs with estimated TCLP values below the regulatory level can be dropped from further evaluation, since the estimated maximum leachability will be less than regulatory levels. Those organic COPCs with estimated TCLP concentrations initially greater than regulatory levels require further evaluation.

The next step of the separate (VOC and SVOC) TCLP reevaluations involve a review of the existing process knowledge associated with any remaining organic COPCs that were not dropped from further evaluation, from the earlier TCLP evaluation. Process knowledge can be used to confirm the absence of specific COPCs wherein there is no reasonable expectation that these specific COPCs should be expected in the V-Tanks waste. Utilization of this process knowledge is reinforced when the existing data fails to show any positive values (i.e. no detects of the COPC above detection levels). Process knowledge that does not suggest the COPC is present plus the lack of any analytical evidence of its presence is a strong indicator that the constituent is not present at concentrations that would make the waste characteristically hazardous, or a threat to human health and the environment. Such process knowledge should include information on the use of these contaminants, whether or not such contaminants were used at TAN, whether or not there is a potential for such a contaminant forming in the tanks, and whether or not its presence in the tanks could ever exceed TCLP regulatory levels.

The process knowledge evaluation will focus on whether or not the remaining organic COPCs were used at TAN, and whether or not an environment exists in the V-tanks that is conducive to their accidental formation at TAN. The process knowledge evaluation will be used to determine the potential for these organic COPCs existing in the V-tanks waste at concentrations exceeding the characteristic levels. If there is a potential for one of the organic COPCs to be present in the V-tank waste, an additional determination will focus on conservatively quantifying the amount of "undetected" contaminant that may be present, and whether such an amount exceeds TCLP concentration limits.

Following this evaluation, an overall review of the reevaluations shall be made, to provide a final determination of which "undetected" organic COPCs (if any) should reasonably be expected to exceed TCLP regulatory levels. Assuming that no remaining organic COPCs exist above TCLP regulatory levels, a hazardous waste determination will be completed that clarifies that the V-tanks waste is only an F001-listed waste that does not exhibit the characteristic of toxicity.

# 5. REFERENCED OR ESTIMATED SAMPLE DATA FOR THE ORGANIC COPCS

As stated previously, a total of eleven organic COPCs have been identified where existing analytical data was insufficient to conclusively state that the waste was not characteristically toxic. The eleven organic COPCs under consideration include four volatile organic COPCs and seven semi-volatile organic COPCs. The eleven organic COPCs, their VOC or SVOC designations, and their potential D-code listings, are as follows:

- Benzene (VOC) D018;
- 1,2-Dichloroethane (VOC) D028;
- 1,1-Dichloroethene (VOC) D029;
- 2,4-Dinitrotoluene (SVOC) D030;
- Hexachlorobenzene (SVOC) D032;
- Hexachlorobutadiene (SVOC) D033;
- Hexachloroethane (SVOC) D034;
- Nitrobenzene (SVOC) D036;
- Pyridine (SVOC) D038;
- 2,4,6-Trichlorophenol (SVOC) D042; and
- Vinyl Chloride (VOC) D043.

The existing V-tank analytical data were analyzed for each of the volatile or semi-volatile organic COPCs. The data includes the estimated "average" concentrations that have been previously estimated for these organic COPCs (those concentrations that were used in the original evaluation, EDF-3795), information on the lowest RDL reported for each V-tank phase material and information on referenced or estimated MDLs for each of these organic COPCs. A discussion of this data is included in Appendix A of this report. The existing and estimated data for each organic COPC is included in Tables A-1, A-2, A-3, and A-4 of Appendix A.

# 6. CHARACTERISTIC REEVALUATION OF VOLATILE ORGANIC COPCS

As previously stated, four volatile organic COPCs have been identified where existing analytical data was insufficient to conclusively state that the waste was not characteristically toxic. The four volatile organic COPCs under consideration, along with their potential D-code listings, are as follows:

- Benzene (D018)
- 1,2-Dichloroethane (D028)
- 1,1-Dichloroethene (D029); and
- Vinyl Chloride (D043).

The purpose of this section of the report is to reevaluate the VOC data for all sludge and supernatant samples, to determine if the use of MDLs could provide a sufficient reduction in estimated TCLP concentrations, within the V-tank waste, to eliminate them from further consideration, with regards to the characteristic hazard designation. The MDLs were used to determine estimated TCLP concentrations for each volatile organic COPC within the consolidated V-tank waste. This concentration was then compared

against the regulatory limits for each volatile COPC, to determine if the revised TCLP concentrations are below regulatory levels for each of these volatile organic COPCs. The additional process knowledge evaluation was not needed for the volatile organic COPCs.

### 6.1 TCLP Concentration Estimates for the Volatile Organic COPCs

The TCLP calculation was performed using the MDL concentrations and volumes of sludge and supernatant in each V-tank, as well as the measured sludge densities and percent solids, in order to define estimated TCLP concentrations of each volatile organic COPC, within consolidated V-tank waste. This approach was based upon EPA guidance for estimating a maximum leachate potential that is included in Appendix C.

The estimated TCLP concentration for the consolidated V-tank waste was calculated on a mass-weighted basis, to define the estimated TCLP concentrations for each volatile organic COPC within the consolidated V-tank waste. The TCLP concentration estimates were then compared against the TCLP regulatory levels for each of the volatile organic COPC under reevaluation, to determine if the new estimates would allow these volatile organic COPCs to be eliminated from further consideration in the characteristic toxicity evaluation.

The results of this TCLP calculation are shown in Table 1 of this EDF. Included in the table is the TCLP regulatory level for each of the "undetected" organic COPCs. Details of the calculations associated with this table are shown in Appendix B of the EDF.

As shown in Table 1, the estimated maximum TCLP concentrations for the four volatile organic COPCs under reevaluation are below TCLP regulatory levels. As a result the four volatile organic COPCs should be eliminated from further consideration in the characteristic toxicity designation of consolidated V-tank waste. There is no need for an overall process knowledge evaluation to be conducted on these four volatile organic COPCs.

The primary reason for the initial contaminant evaluation (EDF-3795) exceeding TCLP regulatory levels for these four VOCs was the use of concentration estimates based on averaging of the RDLs for each contaminant, rather than MDL estimates for each sample. A secondary reason that contributed to high RDLs and MDLs was the extremely high dilutions (10,000) that were required for the V-9 sludge samples. The high dilutions required for V-9 sludge samples were due to the high concentrations of TCE (14,000 mg/kg and 22,000 mg/kg) that were observed in V-9 sludge. The V-9 sludge dilutions were ten times higher than the dilutions used on other V-tank sludge samples, resulting in a ten-fold increase in the RDLs and MDL estimates for the COPCs in V-9 sludge. The high RDLs for these volatile organic

Table 1. Calculated TCLP Estimates for Volatile Organic COPCs in Consolidated V-Tank Waste

Hazardous Constituent	Calculated TCLP Concentrations for Consolidated V-Tank Waste (mg/L)	TCLP Regulatory Limit (mg/L)			
Benzene	0.00 - 0.30	0.50			
1,2-Dichloroethane	0.00 - 0.45	0.50			
1,1-Dichloroethene	0.00 - 0.15	0.70			
Vinyl Chloride	0.002 - 0.15	0.20			

COPCs resulted in an inflated estimate of the concentrations of the four volatile organic COPCs, within consolidated V-tank waste. The end result was TCLP concentration estimates shown in Table 1 that are extremely conservative for each volatile organic COPC in the consolidated V-tank waste.

# 7. CHARACTERISTIC REEVALUATION OF SEMI-VOLATILE ORGANIC COPCS

As stated previously, a total of seven semi-volatile organic COPCs were identified in EDF-3795 as having existing data that was insufficient to conclusively state that the waste was not characteristically toxic. The seven semi-volatile organic COPCs that were identified, along with their potential D-code listings, are as follows:

- 2,4-Dinitrotoluene (D030);
- Hexachlorobenzene (D032);
- Hexachlorobutadiene (D033);
- Hexachloroethane (D034);
- Nitrobenzene (D036);
- Pyridine (D038); and
- 2,4,6-Trichlorophenol (D042).

The purpose of this section of the report is to reevaluate the existing SVOC data for all sludge and supernatant samples, to determine if the SVOC MDLs would also provide a sufficient reduction in estimated TCLP concentrations for these seven semi-volatile organic COPCs within consolidated V-tank waste, thereby eliminating them from further consideration, with regards to the characteristic hazard designation. The MDLs identified for each of these semi-volatile organic COPCs are first used to determine the estimated TCLP concentrations of each COPC, within the consolidated V-tank waste. These concentrations are then compared against the regulatory limits for each semi-volatile COPC, to determine which of the revised TCLP concentrations are below regulatory levels. Those semi-volatile organic COPCs with revised TCLP concentration estimates not below regulatory levels are then submitted to an overall process knowledge evaluation, to see if process knowledge could eliminate them from further consideration.

# 7.1 TCLP Concentration Estimates for the Semi-Volatile Organic COPCs

Using referenced and estimated MDLs for each semi-volatile organic COPC (see Appendix A); a calculation was performed to define the estimated TCLP concentrations for each of the seven semi-volatile organic COPCs in consolidated V-tank waste. The TCLP concentration estimates were then compared against the TCLP regulatory levels for each of the semi-volatile organic COPC under reevaluation, to determine if the new estimates would allow these semi-volatile organic COPCs to be eliminated from further consideration in the characteristic toxicity evaluation.

The TCLP calculation was performed using the same measured volumes of sludge and supernatant, and sludge densities that were used for the volatile organic COPC evaluation. The evaluation also applied the same procedures that were used for TCLP analysis of the VOCs in the previous section involving separation of supernatant from sludge phase, using the "rule of 20" to define TCLP volume for the sludge, and then analyzing liquid and solid phases separately, before recombining).

Results of this TCLP calculation are shown in Table 2 of this EDF. Included in the table is the TCLP regulatory level for each of the "undetected" organic COPCs. Details of the calculations associated with this table are shown in Appendix B of the EDF.

As shown in Table 2, the estimated TCLP concentrations for four of the seven semi-volatile organic COPCs under reevaluation are substantially below TCLP regulatory levels. As a result, these four semi-volatile organic COPCs (i.e., hexachloroethane, nitrobenzene, pyridine, and 2,4,6-trichlorophenol) are eliminated from further consideration, in the characteristic toxicity designation for consolidated V-tank waste. There is also no need for an overall process knowledge evaluation to be conducted on these four semi-volatile organic COPCs.

The current TCLP concentration estimates are still above the regulatory levels for Hexachlorobutadiene; 2,4-Dinitrotoluene; and Hexachlorobenzene requiring further evaluation of historical process knowledge. These detection limit based values are still approximately within the one order of magnitude that EPA has traditionally used for determining whether wastes are in compliance with LDR treatment standards when there are problems with achieving sufficiently low detection levels even though good-faith analytical efforts have been made. However, further consideration of these COPCs for the characteristic hazard designation for consolidated V-tank waste relies on overall process knowledge. This is discussed in the following subsection of this EDF.

# 7.2 Process Knowledge Evaluation for Residual Semi-Volatile Organic COPCs

To eliminate the three remaining semi-volatile organic COPCs (i.e., 2,4-Dinitrotoluene, Hexachlorobenzene, and Hexachlorobutadiene) from further consideration, as to their characteristic toxicity within consolidated V-tank waste, it is necessary to explore the process knowledge of what materials that may have been deposited in the V-Tanks. The residual semi-volatile organic COPCs were looked at in detail, to define their commercial usage, and apply this information with information on the

Table 2. Calculated TCLP Estimates for Semi-Volatile Organic COPCs in Consolidated V-Tank Waste

Hazardous Constituent	Calculated TCLP Concentrations for Consolidated V-Tank Waste (mg/L)	TCLP Regulatory Limit (mg/L)		
2,4-Dinitrotoluene	0.00 - 1.14	0.13		
Hexachlorobenzene	0.00 - 1.39	0.13		
Hexachlorobutadiene	0.00 - 1.56	0.50		
Hexachloroethane	0.00 - 1.68	3.00		
Nitrobenzene	0.00 - 1.52	2.00		
Pyridine	0.00 - 1.91	5.00		
2,4,6-Trichlorophenol	0.00 - 1.13	2.00		

type of operation processes conducted within TAN (the original source for all V-tank wastes). In addition, an evaluation was made of the potential for any of these materials to be formed from inadvertent reactions or decompositions within the V-tanks.

The Merck Index defines Hexachlorobenzene as a material used either in organic syntheses or as a fungicide. In addition, the Agency for Toxic Substances and Disease Registry (ATSDR) identifies Hexachlorobenzene uses as a pesticide, and an ingredient in the manufacture of fireworks, ammunition and synthetic rubber. The history of TAN Operations does not involve any organic syntheses work, fireworks, ammunition, or synthetic rubber. In addition, there is no evidence of the use of Hexachlorobenzene as a pesticide or fungicide at TAN and specifically there is no evidence of this material being discharged to the V-tanks. This rationale (i.e. use of process knowledge) is entirely consistent with the standard approach taken for the primary pesticides and herbicides in the TCLP list (D012-D017). The non-presence of fungicides and pesticides within the V-tank is further supported by actual data obtained from soils sampling around the V-tanks (where pesticides and herbicides would be more readily used), indicating concentrations both below detection levels and detection levels below TCLP regulatory levels (EDF-4619). As there is no reason to believe that these materials might be present in the waste stream, there is no need produce analytical evidence of the material not being present nor any reason to presume a characteristic code being applicable (per EDF-3795).

The ATSDR also says that Hexachlorobenzene could be formed as a by-product while making other chemicals, in the waste streams of chloralkali and wood-preserving plants, and when burning municipal waste. Since TAN has not been involved in any of these operations, it can be safely assumed that there is no reasonable means for Hexachlorobenzene formation in the TAN V-tanks. Therefore, Hexachlorobenzene should not be considered to be present in the consolidated V-tank waste, based upon process knowledge.

2,4-Dinitrotoluene is not referenced in the Merck index. An Internet search for 2,4-Dinitrotoluene found that it is primarily used in the manufacture of polyurethanes (USEPA). It is also used in the munitions industry as a modifier for smokeless powders, as an explosive intermediate, in rubber, chemical and plastics manufacture, and as a plasticizer for moderate and high explosives. 2,4-Dinitrotoluene is present in organic synthesis, dyes, explosives, and as a propellant additive. None of these operations were performed at TAN.

While 2,4-Dinitrotoluene may be formed from combinations of toluene and nitric acid, data from the TAN V-tanks indicates no toluene existing in either the sludge or supernatant phases of the V-tanks and no nitrates present in any V-tanks but Tank V-9. Since both nitrates and toluene have to be present to form 2,4-Dinitrotoluene, it can be safely assumed (via process knowledge) that the RDL and MDL values reported for 2,4-Dinitrotoluene are excessively conservative and that 2,4-Dinitrotoluene should not be considered to be present above TCLP characteristic levels, based upon process knowledge.

Hexachlorobutadiene is also not referenced in the Merck index. The ATSDR indicates that Hexachlorobutadiene is mainly used in the manufacture of rubber compounds. Other uses identified by ATSDR include the manufacture of gyroscopes, and its use as a fungicide, a solvent, a heat transfer liquid, and a hydraulic fluid. None of these uses have been tied to historical operations at TAN. Although solvents, heat transfer liquids, and hydraulic fluids have been used at TAN, there is also no historical evidence involving the use of Hexachlorobutadiene at TAN for any of these purposes.

While there is no evidence of Hexachlorobutadiene usage at TAN, the speculative presence of Hexachlorobutadiene in the V-tanks has been proposed as a result of another reference (Rabovsky, 2000), identifying Hexachlorobutadiene as a by-product in the manufacture of TCE. TCE was used at TAN. The concern is that the Hexachlorobutadiene produced as a by-product of TCE manufacture may have entered the V-tanks as an "undetected" contaminant in the TCE.

Discussions with technical service representatives at Alpha Aesar (a chemical supply company) indicate that the TCE is generally distilled to improve its impurity to 99.99% or greater, even when the material is rated at a purity concentration of only 99+%. Because of the significant differences in boiling point between TCE (87°C) and Hexachlorobutadiene (215°C), it is expected that the nearly all of the Hexachlorobutadiene produced during manufacture will be distilled out of the TCE, before it is readied for use. This is supported by a trace impurity analysis conducted on TCE by J.T. Baker (another chemical supply company), indicating that there was no Hexachlorobutadiene present in their TCE product. Finally, the minimum concentration identified for the TCE product used at TAN is 99+%. Even if all of the non-TCE material in this product was Hexachlorobutadiene (highly unlikely at 10,000 mg/kg maximum), the potential of it existing in consolidated V-tank waste at levels approaching TCLP regulatory concentrations is negligible. This is because the pure TCE product that was used is now in waste at a concentration of 426 mg/kg, an effective dilution of over 2300. If Hexachlorobutadiene were present as a result of the usage of TCE, it would also be subject to the same dilution ratios as the TCE. Since TCE concentration was reduced by a minimum factor of 2300 during the generation process, the Hexachlorobutadiene would have also been reduced by a minimum factor of 2300, to a current V-tank consolidated waste concentration of only 4.3 mg/kg. Since nearly all of the Hexachlorobutadiene would be expected to be in the sludge phase (similar to TCE) the "rule of 20" can be included in this evaluation. Dividing the maximum-determined concentration of Hexachlorobutadiene in V-tank waste (4.3 mg/kg) by the "rule of 20" results in a maximum TCLP concentration for Hexachlorobutadiene in V-tank waste of only 0.22 mg/kg, which is only 44% of the TCLP regulatory standard if it were all leachable from the sludge. This coupled with the fact that the Hexachlorobutadiene was not detected in any of the V-tank samples is sufficient to determine that the waste does not exhibit the characteristics of toxicity for Hexachlorobutadiene.

As a result of the process knowledge evaluation, sufficient data exists to eliminate Hexachlorobenzene, 2,4-Dinitrotoluene, and Hexachlorobutadiene from being present in V-tank waste at concentrations sufficient to exceed the characteristic levels.

#### 8. CONCLUSIONS

The purpose of this reevaluation was to use "conservative" MDLs and general process knowledge to eliminate the eleven "undetected"-organic COPCs from further consideration, as to their exhibition of the characteristic of toxicity within the V-tank waste. The "undetected" organic COPCs under reevaluation included four VOCs and seven SVOCs.

Based on this reevaluation, all eleven of the "undetected"-organic COPCs under reevaluation can be removed from further consideration, as to their characteristic nature within V-tank waste. The eleven contaminants removed from further consideration include:

 All four volatile organic COPCs (benzene, 1,1-Dichloroethene, 1,2-Dichloroethane, and Vinyl Chloride) were eliminated from further consideration (in terms of characteristic toxicity, within consolidated V-tank waste), using conservatively derived MDL estimates, instead of "average" RDLs;

- Four of the seven semi-volatile organic COPCs (Hexachloroethane, Nitrobenzene, Pyridine, and 2,4,6-Trichlorophenol) were eliminated from further consideration, using referenced MDLs instead of "average" RDLs;
- Three of the seven semi-volatile organic COPCs (Hexachlorobenzene, 2,4-Dinitrotoluene, and Hexachlorobutadiene) were eliminated based on a process knowledge review of chemical usage vs. TAN operating process knowledge.

The EDF effectively resolves the ambiguities that have been inherent in previous V-tank waste characterization efforts that resulted primarily from the use of averaged detection limits based upon contractually based reporting limits. Based on the results of this EDF, a hazardous waste determination should be completed designating that the consolidated V-tanks waste should only be regulated as an F001-listed waste. The new hazardous waste determination should use the information in this EDF and EDF-3795 to document that the V-tanks waste is not considered to be characteristically hazardous. This determination will allow remediation to proceed on the F001-listed solvents. Since the waste is not characteristic hazardous, treatment of Underlying Hazardous Constituents is not required. Treatment of PCBs will still be required to the extent necessary, however, to demonstrate no unreasonable risk to human health or the environment as required in the ROD Amendment.

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# APPENDIX A – REVIEW OF ORGANIC COPC DATA FOR THE TCLP CHARACTERISTIC REEVALUATION

The existing V-tank phase data (supernatant and sludge) for each of the organic COPCs is shown in Tables A-1, A-2, A-3, and A-4. The data includes the estimated "average" concentrations that had been previously estimated for these organic COPCs (those concentrations used in the original evaluation, EDF-3795), information on the lowest RDL reported for each V-tank phase material, and information on referenced or estimated MDL data for each organic COPC.

A review of the existing data for the V-tank samples indicated that referenced MDL data was only available for the semi-volatile organic COPCs under reevaluation. Furthermore, there was no referenced MDL data for semi-volatile-organic COPCs within the V-9 supernatant. Where no MDL data is referenced, a decision has been made to use estimated MDL values, rather than using referenced RDL values (see Section 3 of this EDF). All estimated MDLs in Tables A-1 to A-4 are identified via asterisks. Estimation of these MDLs needs to be such that the resulting value has a solid estimation basis for assuring that the resultant estimate is still conservative, in estimating maximum concentration for a particular contaminant.

For semi-volatile organic COPCs within the V-9 supernatant, a decision was made to use the same MDLs that had been referenced for the V-1, V-2 and V-3 supernatant samples. This is because of the equivalent MDL values for V-1, V-2, and V-3 supernatant. Since the V-9 supernatant was analyzed in a similar manner to V-1, V-2, and V-3 supernatant (in terms of percent solids, concentration ratios, and levels of dilution), the referenced MDL for the other supernatant samples should provide a relatively accurate MDL estimate for V-9 supernatant.

For VOCs with estimated concentrations defined by a "u"-flag (meaning that the estimated concentration is below the MDL for that contaminant), an MDL estimate equivalent to 20% of the lowest RDL was used. The basis for this estimate is the same basis identified in the SW846 definition of the EQL (identified in the fifth assumption bullet), which states that the EQL (same as the INEEL RDL) is generally 5-10 times the MDL (EPA 1992). Adjusted MDL estimates were provided for the volatile organic COPCs on nearly all V-tank sludge and supernatant samples. The only exceptions were V-2 and V-3 supernatant data for vinyl chloride, where unflagged total concentrations data was used at the reported concentration.

As shown in Tables A-1 to A-4, the estimated MDLs for the volatile organic COPCs provided the lowest defensible concentrations for use in this reevaluation. The estimated MDLs are typically 12-20% of the "average" concentration data used in the previous volatile organic COPC evaluation (EDF-3795). Use of MDLs is therefore expected to result in substantially lower TCLP concentration estimates for the volatile organic COPCs than were determined in EDF-3795. The data also shows that use of estimated MDLs to approximate TCLP concentrations in the sludge samples (using the "rule of 20") is preferable to using the high detection levels identified for the actual TCLP analyses conducted on the V-1, V-2, and V-3 sludge samples.

Tables A-1 to A-4 also show that referenced and estimated MDLs for semi-volatile organic COPCs are 9-40% of the "average" concentration data used in the previous semi-volatile organic COPC evaluations (EDF-3795). Use of referenced and estimated MDLs is therefore expected to result in substantially lower TCLP concentration estimates, for semi-volatile organic COPCs, than were determined in EDF-3795.

Table A-1. Summary of Concentration Data for Trace Organic COPCs Within Each Phase in V-1.

Organic COPC	Previously Reported Concentration (based on average of RDLs) (mg/kg)	Lowest Reported RDL or Concentration (mg/kg)	Selected MDL Concentration (mg/kg)	Calculated Max. Potential TCLP Concentration (mg/L)
Sludge Data				
Benzene	1.56	0.91u	0.182*	0.0091
1,2-Dichloroethane	1.56	0.91u	0.182*	0.0091
1,1-Dichloroethene	1.56	0.91u	0.182*	0.0091
2,4-Dinitrotoluene	201	76u	18	0.9
Hexachlorobenzene	201	76u	22	1.1
Hexachlorobutadiene	201	76u	24	1.2
Hexachloroethane	201	76u	26	1.3
Nitrobenzene	201	76u	23	1.2
Pyridine	201	76u	30	1.5
2,4,6-Trichlorophenol	201	76u	18	0.9
Vinyl Chloride	1.56	0.91u	0.182*	0.0091
Supernatant Data				
Benzene	0.01	0.01u	0.002*	0.002
1,2-Dichloroethane	0.01	0.01u	0.002*	0.002
1,1-Dichloroethene	0.01	0.01u	0.002*	0.002
2,4-Dinitrotoluene	1.0	1.0u	0.24	0.24
Hexachlorobenzene	1.0	1.0u	0.29	0.29
Hexachlorobutadiene	1.0	1.0u	0.33	0.33
Hexachloroethane	1.0	1.0u	0.35	0.35
Nitrobenzene	1.0	1.0u	0.32	0.32
Pyridine	1.0	1.0u	0.40	0.40
2,4,6-Trichlorophenol	1.0	1.0u	0.24	0.24
Vinyl Chloride	0.01	0.01u	0.002*	0.002

u identified as being below the MDL for this contaminant

<sup>\*</sup> Estimated MDL (20% of lowest RDL)

<u>Table A-2</u>. Summary of Concentration Data for Trace Organic COPCs Within Each Phase in V-2.

Organic COPC	Previously Reported Concentration (based on average of RDLs) (mg/kg)	Lowest Reported RDL or Concentration (mg/kg)	Selected MDL Concentration (mg/kg)	Calculated Max. Potential TCLP Concentration (mg/L)
Sludge Data				
Benzene	0.64	0.6u	0.12*	0.006
1,2-Dichloroethane	0.64	0.6u	0.12*	0.006
1,1-Dichloroethene	0.64	0.6u	0.12*	0.006
2,4-Dinitrotoluene	193	170u	41	2.1
Hexachlorobenzene	193	170u	50	2.5
Hexachlorobutadiene	193	170u	56	2.8
Hexachloroethane	193	170u	60	3.0
Nitrobenzene	193	170u	55	2.7
Pyridine	193	170u	64	3.4
2,4,6-Trichlorophenol	193	170u	41	2.0
Vinyl Chloride	0.64	0.6u	0.12*	0.006
Supernatant Data				
Benzene	0.01	0.01u	0.002*	0.002
1,2-Dichloroethane	0.01	0.01u	0.002*	0.002
1,1-Dichloroethene	0.01	0.01u	0.002*	0.002
2,4-Dinitrotoluene	1.0	1.0u	0.24	0.24
Hexachlorobenzene	1.0	1.0u	0.29	0.29
Hexachlorobutadiene	1.0	1.0u	0.33	0.33
Hexachloroethane	1.0	1.0u	0.35	0.35
Nitrobenzene	1.0	1.0u	0.32	0.32
Pyridine	1.0	1.0u	0.4	0.4
2,4,6-Trichlorophenol	1.0	1.0u	0.24	0.24
Vinyl Chloride	0.02	0.02	NA	0.02

u identified as being below the MDL for this contaminant

<sup>\*</sup> Estimated MDL (20% of lowest RDL)

Table A-3. Summary of Concentration Data for Trace Organic COPCs Within Each Phase in V-3.

Organic COPC	Previously Reported Concentration (based on average of RDLs) (mg/kg)	Lowest Reported RDL or Concentration (mg/kg)	Selected MDL Concentration (mg/kg)	Calculated Max. Potential TCLP Concentration (mg/L)
Sludge Data				
Benzene	0.615	0.6u	0.12*	0.006
1,2-Dichloroethane	0.615	0.6u	0.12*	0.006
1,1-Dichloroethene	0.615	0.6u	0.12*	0.006
2,4-Dinitrotoluene	180	100u	24	1.2
Hexachlorobenzene	180	100u	29	1.4
Hexachlorobutadiene	180	100u	33	1.6
Hexachloroethane	180	100u	35	1.8
Nitrobenzene	180	100u	32	1.6
Pyridine	180	100u	40	2.0
2,4,6-Trichlorophenol	180	100u	24	1.2
Vinyl Chloride	0.615	0.6u	0.12*	0.006
Supernatant Data				
Benzene	0.01	0.01u	0.002*	0.002
1,2-Dichloroethane	0.01	0.01u	0.002*	0.002
1,1-Dichloroethene	0.01	0.01u	0.002*	0.002
2,4-Dinitrotoluene	1.0	1.0u	0.24	< 0.24
Hexachlorobenzene	1.0	1.0u	0.29	< 0.29
Hexachlorobutadiene	1.0	1.0u	0.33	< 0.33
Hexachloroethane	1.0	1.0u	0.35	< 0.35
Nitrobenzene	1.0	1.0u	0.32	< 0.32
Pyridine	1.0	1.0u	0.40	< 0.40
2,4,6-Trichlorophenol	1.0	1.0u	0.24	<0.24
Vinyl Chloride	0.011	0.011	NA	0.011

u identified as being below the MDL for this contaminant

<sup>\*</sup> Estimated MDL (20% of lowest RDL)

Table A-4. Summary of Concentration Data for Trace Organic COPCs Within Each Phase in V-9.

Organic COPC	Previously Reported Concentration (based on average of RDLs) (mg/kg)	Lowest Reported RDL or Concentration (mg/kg)	Selected MDL Concentration (mg/kg)	Calculated Max. Potential TCLP Concentration (mg/L)
Sludge Data				
Benzene	250	250u	50*	2.5
1,2-Dichloroethane	380	380u	76*	3.8
1,1-Dichloroethene	120	120u	24*	1.2
2,4-Dinitrotoluene	140	130u	31	1.6
Hexachlorobenzene	140	130u	39	1.9
Hexachlorobutadiene	140	130u	43	2.2
Hexachloroethane	140	130u	47	2.3
Nitrobenzene	140	130u	42	2.1
Pyridine	140	130u	53	2.7
2,4,6-Trichlorophenol	140	130u	31	1.6
Vinyl Chloride	120	120u	24*	1.2
Supernatant Data				
Benzene	17	17u	3.4*	3.4
1,2-Dichloroethane	25	25u	5*	5
1,1-Dichloroethene	11	11u	2.2*	2.2
2,4-Dinitrotoluene	0.01	0.01u	0.0024*	< 0.0024
Hexachlorobenzene	0.01	0.01u	0.0029*	< 0.0029
Hexachlorobutadiene	0.01	0.01u	0.0033*	< 0.0033
Hexachloroethane	0.01	0.01u	0.0035*	< 0.0035
Nitrobenzene	0.01	0.01u	0.0032*	< 0.0032
Pyridine	0.01	0.01u	0.004*	< 0.004
2,4,6-Trichlorophenol	0.01	0.01u	0.0024*	< 0.0024
Vinyl Chloride	13	13u	2.6*	2.6

identified as being below the MDL for this contaminant Estimated MDL (20% of lowest RDL)

The data also shows that referenced MDLs are generally only 24-40% of the minimum RDLs for each semi-volatile organic COPC under reevaluation. Such percentages are higher than the 20% value "conservatively" used to define estimated MDLs for the volatile organic COPCs with non-referenced MDLs. However, the higher RDL:MDL ratios experienced by the semi-volatile organic COPCs are a direct result of the limited concentrations found in the SVOC samples, due to the high oil concentrations in these samples. These values are a result of the problems inherent in SVOC analysis of oily waste. These values are still valid even though they fall outside the standard RDL:MDL ratios, referenced by EPA, of 10-20%.

Following this evaluation, each Appendix A-table provides an estimated TCLP concentration for the various sludge or supernatant samples associated with this evaluation. For sludge samples, the estimated TCLP concentration is calculated by simply dividing the adjusted MDL for that sample by 20 (according to the "rule of 20"). For supernatant samples, the TCLP concentration is simply defined as the totals concentration for each organic COPC within the supernatant samples. Such ratios are within the guidelines associated with using totals concentrations to approximate TCLP concentrations for slurries, per Section 309 of Chapter 20 of the RCRA Regulations and Keyword Index (Aspen Law and Business, 2003), provided the sludge samples can be analyzed for TCLP without being able to separate additional liquid from the sludge samples. This condition was confirmed as part of the preliminary TCLP analyses conducted on V-1, V-2 and V-3 sludges (Johnson, HCJ-146-02, 2002).

## APPENDIX B – SPREADSHEET TCLP CALCULATIONS IN SUPPORT OF EDF-4885

<u>Table B-1</u>. Waste Analysis for V-Tank Sludges.

Waste	Hazardous	TCLP		Tank V	-1 Sludge			Tank V-2 Sludge				Tank V	/-3 Sludge			Tank V	Tank V-9 Sludge			
Code	Constituent	Limit	Min. RDL	MDL	Adj. MDL	TCLP Est.	Min. RDL	MDL	Adj. MDL	TCLP Est.	Min. RDL	MDL	Adj. MDL	TCLP Est.	Min. RDL	MDL	Adj. MDL	TCLP Est.		
		(mg/L)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/L)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/L)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/L)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/L)		
D018	Benzene	0.50	0.91		0.182	0.0091	0.6		0.12	0.006	0.6		0.12	0.006	250		50	2.5		
D028	1,2-Dichloroethane	0.50	0.91		0.182	0.0091	0.6		0.12	0.006	0.6		0.12	0.006	380		76	3.8		
D029	1,1-Dichloroethylene	0.70	0.91		0.182	0.0091	0.6		0.12	0.006	0.6		0.12	0.006	120		24	1.2		
D030	2,4-Dinitrotoluene	0.13	76	0.079	17.94	0.8971	170	0.079	41.08	2.054	100	0.079	23.81	1.190	130	0.079	31.74	1.6		
D032	Hexachlorobenzene	0.13	76	0.096	21.80	1.0902	170	0.096	49.92	2.496	100	0.096	28.93	1.447	130	0.096	38.57	1.9		
D033	Hexachlorobutadiene	0.50	76	0.108	24.53	1.2265	170	0.108	56.16	2.808	100	0.108	32.55	1.627	130	0.108	43.39	2.2		
D034	Hexachloroethane	3.00	76	0.116	26.35	1.3173	170	0.116	60.32	3.016	100	0.116	34.96	1.748	130	0.116	46.60	2.3		
D036	Nitrobenzene	2.00	76	0.105	23.85	1.1924	170	0.105	54.60	2.730	100	0.105	31.65	1.582	130	0.105	42.18	2.1		
D038	Pyridine	5.00	76	0.132	29.98	1.4990	170	0.132	68.64	3.432	100	0.132	39.78	1.989	130	0.132	53.03	2.7		
D042	2,4,6-Trichlorophenol	2.00	76	0.078	17.72	0.8858	170	0.078	40.56	2.028	100	0.078	23.51	1.175	130	0.078	31.34	1.6		
D043	Vinyl Chloride	0.20	0.91		0.182	0.0091	0.6		0.12	0.006	0.6		0.12	0.006	120		24	1.2		
	SVOC Adjustment F	actors																		
	Sample Wt (g):			1.738				1.202				2.212				1.524				
% Moisture: 24					52				55				51							
Conc. Extract Volume (uL):			10000				10000				10000				10000					
Std Conc. Extract Volume (uL):			1000				1000				1000				1000					
	Dilution Factor:			1				1				1				1				

Italics - Detection limit value

<u>Table B-2</u>. Waste Analysis for V-Tank Supernatants.

Waste	Hazardous	TCLP	Tanl	Tank V-1 Supernatant			V-2 Suj	pernatant	Tan	k V-3 Supe	ernatant	Tank V-9 S	upernatant
Code	Constituent	Limit	RDL	MDL	Adj. MDL	RDL	MDL	Adj. MDL	RDL	MDL	Adj. MDL	RDL	Adj. MDL
		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
D018	Benzene	0.50	0.01		0.002	0.01		0.002	0.01		0.002	17	3.4
D028	1,2-Dichloroethane	0.50	0.01		0.002	0.01		0.002	0.01		0.002	25	5.0
D029	1,1-Dichloroethylene	0.70	0.01		0.002	0.01		0.002	0.01		0.002	11	2.2
D030	2,4-Dinitrotoluene	0.13	1	0.0024	0.24	1	0.0024	0.24	1	0.0024	0.24	0.01	0.0024
D032	Hexachlorobenzene	0.13	1	0.0029	0.29	1	0.0029	0.29	1	0.0029	0.29	0.01	0.0029
D033	Hexachlorobutadiene	0.50	1	0.0033	0.33	1	0.0033	0.33	1	0.0033	0.33	0.01	0.0033
D034	Hexachloroethane	3.00	1	0.0035	0.35	1	0.0035	0.35	1	0.0035	0.35	0.01	0.0035
D036	Nitrobenzene	2.00	1	0.0032	0.32	1	0.0032	0.32	1	0.0032	0.32	0.01	0.0032
D038	Pyridine	5.00	1	0.004	0.4	1	0.004	0.4	1	0.004	0.4	0.01	0.004
D042	2,4,6-Trichlorophenol	2.00	1	0.0024	0.24	1	0.0024	0.24	1	0.0024	0.24	0.01	0.0024
D043	Vinyl Chloride	0.20	0.01		0.002	0.02		0.02	0.011		0.011	13	2.6

### **SVOC Adjustment Factors**

Italics - Detection limit value Sample Vol (mL): 10 Note: same volume for V-1 through V-3

Std Vol (mL): 1000

Dilution Factor: 1

<u>Table B-3</u>. Measured Tank Volumes Used in TCLP Calculations.

Property	Tank	Tank	Tank	Tank	Consolidated
	V-1	V-2	V-3	V-9	Waste
Volume of Supernatant (L)	4406	4307	28997	265	37975
Volume of Sludge (L)	1968	1734	2468	946	7116
Sludge Density (kg/L)	1.017	1.020	1.018	1.126	1.033
Weight of Sludge (kg)	2002	1769	2512	1065	7348

<u>Table B-4</u>. Calculated TCLP Values for the Consolidated V-Tank Waste.

Waste	Hazardous	TCLP Limit	Tank	Tank	Tank	Tank	All
Code	Constituent	(mg/L)	V-1	V-2	V-3	V-9	Tanks
D018	Benzene	0.50	0.0084	0.0056	0.0045	2.51	0.30
D028	1,2-Dichloroethane	0.50	0.0084	0.0056	0.0045	3.81	0.45
D029	1,1-Dichloroethylene	0.70	0.0084	0.0056	0.0045	1.21	0.15
D030	2,4-Dinitrotoluene	0.13	0.83	1.86	0.84	1.57	1.14
D032	Hexachlorobenzene	0.13	1.01	2.26	1.02	1.90	1.39
D033	Hexachlorobutadiene	0.50	1.14	2.54	1.15	2.14	1.56
D034	Hexachloroethane	3.00	1.22	2.73	1.24	2.30	1.68
D036	Nitrobenzene	2.00	1.11	2.47	1.12	2.08	1.52
D038	Pyridine	5.00	1.39	3.10	1.41	2.62	1.91
D042	2,4,6-Trichlorophenol	2.00	0.82	1.83	0.83	1.55	1.13
D043	Vinyl Chloride	0.20	0.0084	0.0075	0.0078	1.22	0.15

# APPENDIX C – EPA GUIDANACE ON ESTIMATING MAXIMUM POTENTIAL LEACHATE CONCENTRATIONS BASED ON TOTALS

The following is based on EPA responses to questions as documented in Chapter 20 Question 309 of the RCRA Regulations and Keyword Index: (Aspen Law & Business, 2003).

# RCRA-309 Use of Total Waste Analysis in Toxicity Characteristic Determinations

**Question:** A generator suspects that his waste may exhibit the toxicity characteristic and thus be subject to regulation as a RCRA hazardous waste. Since he is unsure of the types and concentrations of hazardous contaminants present in the waste, he performs a total waste analysis. Can he use the results of the total waste analysis to make a toxicity characteristic determination, or must he perform Method 1311, the toxicity characteristic leaching procedure (TCLP), to determine the waste's regulatory status?

Answer: While a toxicity characteristic determination under § 261.24 typically involves application of the TCLP followed by analysis of the TCLP extract, a generator may be able to use total waste analysis to demonstrate that a waste does not exhibit the toxicity characteristic. Section 1.2 of the TCLP states, "If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run." This analysis can provide the generator with a convenient and cost-effective means of determining if he needs to run the TCLP in order to definitively characterize a waste.

The means for using total waste analysis results to make a toxicity characteristic determination reflect TCLP methodology and, therefore, vary depending on whether the waste is defined as a liquid, a solid, or a dual-phase waste. Under the TCLP, liquid wastes (i.e., those wastes that contain less than 0.5% dry solids) do not require extraction. The waste, after filtration, is defined as the TCLP extract (Method 1311, Section 2.1). A generator can, therefore, characterize a liquid waste by filtering the waste, measuring total constituent concentrations in the resulting filtrate, and comparing these concentrations to the appropriate regulatory limits under § 261.24.

Wastes which are either 100% solid (i.e., wastes that contain no filterable liquid (Method 1311, Section 7.1.1.1) or which contain both a liquid and a solid component require conversion of total waste analysis data to estimates of constituent concentrations in the TCLP extract, or maximum theoretical leachate concentrations. For instance, to evaluate the regulatory status of a 100% solid, a generator can simply divide each total constituent concentration by 20 and then compare the resulting maximum theoretical leachate concentration to the appropriate regulatory limit (the division factor reflects the 20-to-1 ratio of extraction fluid to solid used in the TCLP). If no maximum theoretical leachate concentration equals or exceeds the appropriate regulatory limit, the solid cannot exhibit the toxicity characteristic, and the TCLP need not be run.

The generator of a dual-phase waste (i.e., a waste which has both a solid and a filterable liquid component) can perform a total waste analysis on the liquid and solid portions and calculate maximum theoretical leachate concentrations for the waste as a whole by combining results mathematically through use of the following formula:

$$[AxB] + [CxD]$$
  
----- = M  
 $B + [20 L/kg x D]$ 

where:

A = concentration of the analyte in the liquid portion of the sample (mg/L)

B = volume of the liquid portion of the sample (L)

C = concentration of the analyte in the solid portion of the sample (mg/kg)

D = weight of the solid portion of the sample (kg), and

M = maximum theoretical leachate concentration (mg/L).

#### For example:

A generator who receives the results of a total waste analysis wishes to determine if his waste exhibits the toxicity characteristic for lead. Since he knows the lead concentration in each phase of the waste (0.023 mg/L in the liquid phase, 85 mg/kg in the solid phase), the volume of the liquid phase (0.025 L), and the weight of the solid phase (0.075 kg), he can calculate the waste's maximum theoretical leachate concentration:

$$[AxB] + [CxD] = [0.023 \text{ mg/L } x 0.025 \text{ L}] + [85 \text{ mg/kg } x 0.075 \text{ kg}] \\ B + [20 \text{ L/kg } x \text{ D}] = 0.025 \text{ L} + [20 \text{ L/kg } x 0.075 \text{ kg}] \\ = 4.18 \text{ mg/L}$$

Because the 4.18-mg/L maximum theoretical leachate concentration is below the 5.0 mg/L regulatory limit, the generator determines that the waste cannot exhibit the toxicity characteristic for lead.

If maximum theoretical leachate concentrations are less than the applicable limits under § 261.24, the waste does not exhibit the toxicity characteristic and the TCLP need not be run. If, on the other hand, total waste analysis data yield a maximum theoretical leachate concentration that equals or exceeds the toxicity characteristic threshold, the data cannot be used to conclusively demonstrate that the waste does not exhibit the toxicity characteristic. The generator may have to conduct further testing to make a definitive toxicity characteristic determination.